

SHORT
COMMUNICATIONS

3-Oxapentane-1,5-diselenol

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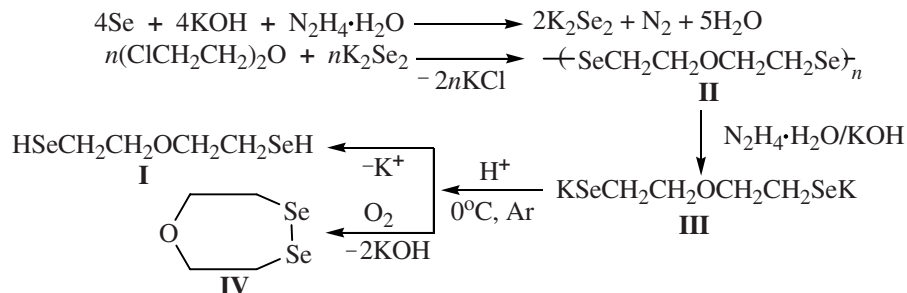
Selenium analogs of thiols are still rare and difficultly accessible compounds [1]. 3-Oxapentane-1,5-diselenol (**I**) is not described in the literature, but the presence in its molecule of an ether oxygen and two highly reactive SeH moieties gives a hope that it would be useful for the synthesis of efficient complexing ligands, in particular, of selenium analogs of crown ethers. The sulfur analog of compound **I**, 3-oxapentane-1,5-dithiol, was successfully applied to the synthesis of such sulfur-containing ligands [2].

We formerly synthesized 1,3-propanediselenol [3] by reductive cleavage of selenokol prepared by reaction of 1-bromo-3-chloropropane in a basic reducing system hydrazine hydrate alkali. An analogous approach was used in the synthesis of compound **I**.

β,β' -Dichlorodiethyl ether (chlorex) was brought into the reaction with selenium in a water-hydrazine alkali solution. As a result we obtained in 66% oligomer **II** as a viscous black fluid. Selenokol **II** introduced into a system hydrazine hydrate-alkali suffered a reductive cleavage at the Se-Se bond. On acidifying the solution of diselenolate **III** obtained we isolated and identified two compounds: diselenol **I** (8%) and 1-oxa-4,5-diselenapentane (**IV**) (45%).

The considerable yield of compound **IV** demonstrates that diselenol **I** is prone to oxidation.

3-Oxapentane-1,5-diselenol (I). In a mixture of 5 ml of hydrazine hydrate, 20 ml of water, and 5.6 g (100 mmol) of KOH was dissolved 7.9 g (100 mmol) of selenium at 80–85°C. To the solution obtained at 60–65°C 7.9 g (55 mmol) of chlorex was added. We obtained 7.61 g (66%) of oligomer **II**. 5 g (22 mmol) of oligomer obtained was dissolved in a mixture of 15 ml of hydrazine hydrate and 5 g (89 mmol) of KOH at 75–80°C and was heated for 2.5 h. The reaction mixture cooled to 25°C was poured in a flow of argon on ice with 40 ml of concn. HCl added. The formed oily substance was extracted with CH_2Cl_2 , the extract was flushed with argon and dried with magnesium sulfate. The residue after evaporating the solvent (2.66 g) was a mixture of two compounds **I** and **IV** that were separated by fractional distillation in a vacuum. The fraction of bp 105°C (2 mm Hg) is practically pure diselenol **I**. Light yellow fluid. IR spectrum: $\nu_{\text{Se-H}}$, 2295 cm^{-1} . ^1H NMR spectrum (CDCl_3), δ , ppm: –0.46 t (SeH, $^1J_{\text{Se-H}}$ 46.71 Hz), 2.74 m (CH_2Se), 3.66 t (OCH_2). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 16.76 (CH_2Se , $J_{\text{C-Se}}$ 51.23 Hz), 72.35 (CH_2O). Mass spectrum, m/z (I_{rel} , %): $[\text{M}]^{+}$ is absent, 109 and 108 (23)



$[\text{C}_2\text{H}_5\text{Se}]^+$, $[\text{C}_2\text{H}_4\text{Se}]^+$, 95 and 93 (18) $[\text{CH}_3\text{Se}]^+$, $[\text{CHSe}]^+$, 81 and 80 (24) $[\text{HSe}]^+$, $[\text{Se}]^+$. Found, %: C 20.78; H 4.18; Se 67.42. $\text{C}_4\text{H}_{10}\text{OSe}_2$. Calculated, %: C 20.69; H 4.31; Se 68.09.

1-Oxa-4,5-diselenaepane (IV) is the main component in the fraction of bp 125–130°C (2 mm Hg). Yellow oily substance. In the IR spectrum the band $\nu_{\text{Se-H}}$ 2295 cm^{-1} is absent. ^1H NMR spectrum (CDCl_3), δ , ppm: 3.13 t (CH_2Se), 3.78 t (CH_2O). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 29.30 (CH_2Se , $J_{\text{C-Se}}$ 74.50 Hz), 70.75 (CH_2O). Mass spectrum, m/z (I_{rel} , %): 232 (<1) $[\text{M}]^+$, 160 (8) $[\text{Se}_2]^+$, 108 and 107 (11) $[\text{C}_2\text{H}_4\text{Se}]^+$, $[\text{C}_2\text{H}_3\text{Se}]^+$, 95 and 93 (21) $[\text{CH}_3\text{Se}]^+$, $[\text{CHSe}]^+$, 80 (18) $[\text{Se}]^+$. Found, %: C 21.61; H 3.69; Se 67.68. $\text{C}_4\text{H}_8\text{OSe}_2$. Calculated, %: C 20.87; H 3.48; Se 68.68.

IR spectra were recorded on a spectrophotometer Bruker IFS-25 from thin films, NMR spectra, on

a spectrometer Bruker DPX-400, mass spectra, on a Shimadzu GCMS-QP5050A instrument, quadrupole mass analyzer, electrons energy 70 eV, the given values of m/z (I_{rel} , %) for selenium-containing ions correspond to the isotope ^{80}Se .

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